REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-98-

0539

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	26 June 1998	Final 15 January 1994-14 February 1998

4. TITLE AND SUBTITLE

(U) Modeling Study to Evaluate the Ionic Mechanism of Soot Formation

5. FUNDING NUMBERS

PE - 61102F
PR - 2308
SA - BS
C - F49620-94-C-0014

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8. PERFORMING ORGANIZATION REPORT NUMBER

TP-569

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NA
110 Duncan Avenue, Suite B115
Bolling AFB DC 20332-0001

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

19980730 145

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Development of a thermochemical data base containing seventy cations of possible importance in soot formation was completed. The results were generalized for the estimation of the Gibbs energies of cations not included in the data base. The chemical kinetic model was expanded to include the chemiionization step by adding concentration profiles of O atoms and electronically excite CH as inputs to the program. The computer code was modified to include the chemiionization step, electron attachment and cation-anion recombination. Under some conditions the computer model and experiment were in excellent agreement, but questions remained. Analysis performed in this project indicated that gas sample cooling by the mass spectrometer sampling cone could have, for some cations, caused reactions to occur so that the mass analysis indicated a different ion from that in the flame. Calculations showed that energy liberated in rapid ion-molecule reactions accumulates in the product cation complicating the reaction kinetics. A survey of published flame measurements found that only ions dramatically change at soot threshold, but no explanation for this change was identified. The possible importance of choosing a neutral or ionic mechanism on the results of modeling soot formation in turbulent flow was considered.

14. SUBJECT TERMS

Soot Formation, Ions in Flames, Ions, Theromochemistry, Ion-molecule Reactions, Modeling

15. NUMBER OF PAGES

24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

TP-569

MODELING STUDY TO EVALUATE THE IONIC MECHANISM
OF SOOT FORMATION

FINAL REPORT

For the Period 15 January 1994 to 14 February 1998

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Contract F49620-94-C-0014

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I. INTRODUCTION

The objective of this study was to evaluate the ionic mechanism of soot formation in flames, and compare the ionic mechanism with the free radical mechanism. This research addressed: (1) the nucleation step, (2) the mechanism of formation and removal of the large cations observed in flames, and (3) the growth of cations to produce soot. The main tool was computer modeling and comparison of the calculated results with experimental results. Wherever possible, experimental data relative to soot formation were interpreted by both the ionic and the free radical mechanisms.

Before proceeding with the modeling study it was necessary to develop a thermochemical database for cations, especially at high temperatures because the necessary data were not available. This proved to be a major endeavor. It was also necessary to develop a detailed reaction mechanism including ion-molecule reactions and ion-electron dissociative recombination reactions. This proved to be a difficult problem because there are no experimental data on ion-molecule reactions at flame temperatures. Available experimental data at ambient temperatures were used and supplemented by Langevin theory calculations for ion-molecule rate coefficients. Langevin theory is in excellent agreement with experimental data and it does not predict a temperature effect. It turned out that thermochemistry was more important than reaction rates because the reaction rates are so fast and for many ion-molecule reactions, thermochemistry reverses the direction of the reaction at the high temperature of the flame, above about 1800 K, because of entropy effects. This observation led to the speculation that the mass spectrometer sampling probe might cool the sampled gas, shifting the observed gas composition to a composition more appropriate at lower temperatures. The influence of the sampling probe on the temperature of the gas entering the sampling probe was thus modeled and the model results indicated that this could be a significant effect. This effect was thus incorporated into the ionic model of cation growth in flames, further complicating interpretation of computer results and comparison with experiment..

The standard flame code was modified by Prof Egolfopoulos (University of Southern California at Los Angles) to handle cations. All of these developments went on in an iterative fashion. Thermochemistry and reaction mechanisms were developed to the point where they could be incorporated into the flame code. Then when the flame code was run, the need for additional data was identified, so new information was developed and added to the data bases. In many cases when we ran with the modified data bases, new difficulties with the computer code were identified and fixed. A major code problem was the inclusion of ambipolar diffusion (combined diffusion of cations of varying size with electrons) in the code. At several times in the course of this work excellent agreement was found between model results and experiment. Then, upon examining the results in detail, an inconsistency would be found, which, when addressed, caused the agreement to become less satisfactory.

In this final report, the status of the work is reported. There is much more to be done to understand the ionic mechanism of soot formation, but real progress has been made and as evidence continues to mount supporting the ionic mechanism, new problems requiring attention have been identified. The availability of thermochemical and reaction data bases developed in this program will make it easier for others to continue this work. There are still a large number of publications which

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should be prepared and submitted to the journals to make the results available to the scientific community. Because of the iterative nature of the work, these journal articles could not be submitted in series. Thus the principal investigator is preparing, on his own time, publication of the results. These journal submissions will include papers describing: (1) thermochemistry of large cations; (2) the development of the reaction mechanism with kinetic parameters; (3) sample cooling by the mass spectrometer sampling probe; and (4) calculation of the ion profiles in the well studied acetylene / oxygen flame and comparison of the calculated results with experimental data. This acetylene / oxygen flame has been the "standard flame" for soot studies by many investigators, so there are a lot of data available. Unfortunately, it was recently discovered in this study that the "standard flame" is not a typical hydrocarbon flame. In most hydrocarbon / air (or oxygen) flames, soot formation is a supra-equilibrium process, occurring at C/O < 1.0, where stoichiometry predicts soot should form, i.e. the concentration of soot is in excess of equilibrium. In the above acetylene / oxygen flame, soot is produced at less than equilibrium concentrations, and appears at C/O = 1.0 !

Other aspects of soot formation were identified in this program and they will be discussed briefly in this report. (1) The mechanism determining the soot threshold is not understood and has received very little attention. Interestingly, at the soot threshold nothing in the flame changes except the ion concentration and the size of the ions. (2) Because ion-molecule reactions are highly exoergic (enthalpy) and frequently exergonic (Gibbs energy) and very fast, the reaction energy does not equilibrate with the bath gas. The excess energy accumulates in the growing ions and thus affects the succeeding steps. An increase in the Gibbs energy of a reacting cation, involved in a highly exergonic reaction has no effect. However for those reactions for which the Gibbs energy changes from negative to positive at the higher temperatures, it increases the net forward reaction rate. These kinds of reactions are common in the cation growth mechanism of soot formation. There is also a counter effect. Accumulation of energy may also cause the cations to dissociate, thus slowing the growth process. (3) Consideration of the relaxation times for ion-molecule reactions and neutral reactions hypothesized to be important in soot formation with relaxation times in turbulent flow indicates that the choice of soot formation mechanism (ionic or free radical) is important in modeling soot formation in turbulent flow. These concepts will be presented briefly in this report; they offer future lines for research.

II. THERMOCHEMICAL DATA BASE

Work on the thermochemical database has been completed, and it should soon be submitted to the Journal of Physical Chemistry. Its submission has been hampered by the departure of one of the authors, who is no longer available for consultation. Recent work in this program on the database was motivated by the desire to add some partially saturated fused ring compounds to the database. For the unsaturated single ring compounds, cyclohexene, 1,3-cyclohexadiene and 1,4-hexadiene, data were available to calculate the thermochemical properties by statistical mechanics. Benson group values [Benson, 1976] were also used to calculate these quantities for a straight chain hydrocarbon. The difference between the two calculated values was assumed to be the group value correction for a ring, These group values were then used to estimate the thermochemistry of the fused ring compounds.

The thermochemistry database has been further updated and examined in an attempt to generalize the results to estimate values for ions not treated in this program, and to extend the results to larger ions. For this purpose the positive ions were divided into three main classes defined as:

Cations, R^+, conceived as being produced by removing a hydride ion from a neutral molecule:

$$RH \Rightarrow R^+ + H^- \qquad (R1)$$
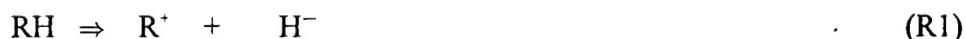
where R represents a hydrocarbon free radical or PAH (polycyclic aromatic hydrocarbon) radical, H represents hydrogen.

Free Radical Cations, $RH^{+\bullet}$, conceived as being produced by removing an electron, e^-, from a neutral molecule:

$$RH \Rightarrow RH^{+\bullet} + e^- \qquad (R2)$$

Protonated Molecular Cations, RH_2^+, conceived as being produced by adding a proton to a neutral molecule:

$$RH + H^+ \Rightarrow RH_2^+ \qquad (R3)$$

To generalize the results so that thermochemical properties of cations not considered in this study could be estimated, the Gibbs energy values, $\Delta_f G$, were correlated by multiple regression analysis with the total number of carbon atoms. The value r^2 is the coefficient of determination for the results of a nonlinear curve fit. Values of r^2 near 1 indicate that the equation is a good description of the relation between the independent and dependent variables.[Hoerl, A. E. et al, 1984]. An example of the correlation for cations at 2000 K is shown in Fig. 1. The equation fitting this correlation is:

$$\Delta_f G_{2000} = 51.348\, n + 919.62 \text{ kJ/mol}, \quad r^2 = 0.935 \qquad (1)$$

where n is the number of carbon atoms in the ion.

For free radical cations the equation is:

$$\Delta_f G_{2000} = 33.231\, n + 1130.7 \text{ kJ/mol}, \quad r^2 = 0.923 \qquad (2)$$

For protonated molecular cations the equation is:

$$\Delta_f G_{2000} = 48.55\, n + 956.79 \text{ kJ/mol}, \quad r^2 = 0.949 \qquad (3)$$

The availability of this data base will make it possible for others to model flame ionization phenomena when large cations are involved such as in soot formation and the production of fullerenes in flames This data base will also be useful to astrochemists because the same growth of cations is postulated to occur in interstellar space as occurs in hydrocarbon flames.
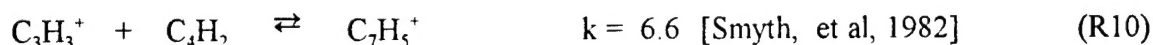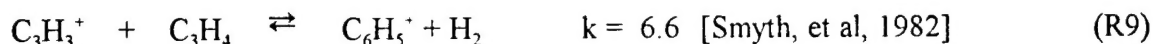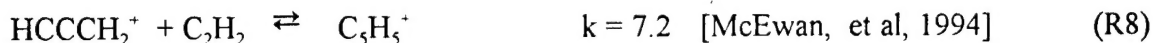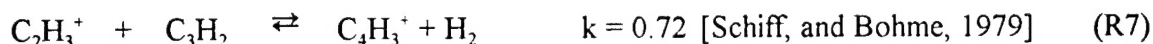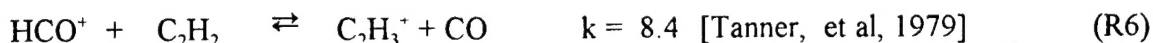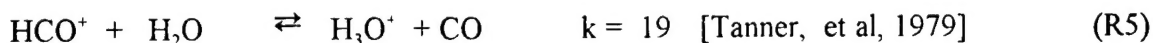
III. CHEMICAL KINETICS MODEL

Throughout this program the chemical kinetics model has been revised by choice of elementary reactions to employ, and in some cases, by changing the reaction rate coefficients and especially the temperature coefficients, because, as pointed out in the introduction, there are no good experimental or theoretical bases for the temperature coefficient of an ion-molecule reaction involving PCAH cations at flame temperatures. As previously reported, the Langevin reaction rates are so fast as to be less important than thermochemistry in determining the growth of cations. Thermochemistry dominates by essentially controlling the direction of the reaction. Ion-molecule reactions, by convention, are generally reported to proceed in the direction of negative Gibbs energy of reaction and that convention has been followed here for the direction at room temperature. However at flame temperatures the Gibbs energy of reaction sometimes becomes positive due to entropy effects. Then, the direction of the reaction is reversed. For intermediate values of Gibbs energy the net direction and rate are still determined by the thermochemistry which, in essence, appears as an activation energy. One of the phenomena this work has explained is the observation that the rates of ion-molecule reactions, for a given homologous series, are frequently correlated with the enthalpy of reaction. Actually, the correlation should be made with the Gibbs energy of reaction rather than the enthalpy, but the two energies are nearly equivalent near room temperature where the correlations are made.

In the chemical mechanism, neutral species mechanisms were originally avoided by inputting a set of experimentally measured neutral species profiles and experimentally measured ion profiles for the two small ions, $C_3H_3^+$ and $C_6H_5^+$ for which experimental data are available. The electron concentration was then equated to the initial total ion concentration, which meant that neither ion-electron recombination nor the formation of negative ions could be included in the mechanism. This short coming has been corrected by including the chemiionization reaction (Reaction R4 below) in the mechanism. Since experimental profiles for the reactants, electronically excited CH, CH*, and oxygen atoms are not available for the flame of interest, and to avoid encumbering the calculations with a lot of neutral reactions, the profiles for CH* and O were estimated. The CH* profile was estimated from experimental observations of CH* profiles in other flames [Jessen and Gaydon, 1969, Calcote, 1981, and Calcote, 1972], and was described using three parameters: the maximum CH* concentration, the distance from the burner at which this concentration peaks, and the width of the concentration profile, which was assumed to be parabolic. This must be considered as an assumed parameter, with the understanding that eventually it should be measured or calculated. The O atom profile was calculated from experimental data for H_2, OH and H, assuming the equilibrium: $H_2 + O \rightleftharpoons OH + H$. The data was taken from Vovelle [1989], who made measurements in the same flame. The three CH* parameters were varied until the experimental profiles of the two ions, $C_3H_3^+$ and $C_6H_5^+$, previously used to initiate the calculation, were reasonably well duplicated.

The rate coefficient for the chemiionization reaction was taken from Cool. and Tjossem 1984]:

$$CH^* + O \quad \rightleftharpoons \quad HCO^+ \qquad\qquad k = 3.3 \times 10^{13} \ cm^3 \ mol^{-1} \ s^{-1} \qquad (R4)$$
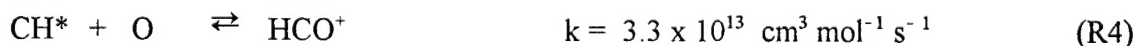
To produce the initial low mass ions from HCO^+, experimental rate coefficients were also taken from the literature when available. Some of the experimental values, in units of 10^{14} cm^3 s^{-1} are reproduced here:

$$HCO^+ + H_2O \rightleftarrows H_3O^+ + CO \qquad k = 19 \text{ [Tanner, et al, 1979]} \qquad \text{(R5)}$$

$$HCO^+ + C_2H_2 \rightleftarrows C_2H_3^+ + CO \qquad k = 8.4 \text{ [Tanner, et al, 1979]} \qquad \text{(R6)}$$

$$C_2H_3^+ + C_3H_2 \rightleftarrows C_4H_3^+ + H_2 \qquad k = 0.72 \text{ [Schiff, and Bohme, 1979]} \qquad \text{(R7)}$$

$$HCCCH_2^+ + C_2H_2 \rightleftarrows C_5H_5^+ \qquad k = 7.2 \text{ [McEwan, et al, 1994]} \qquad \text{(R8)}$$

$$C_3H_3^+ + C_3H_4 \rightleftarrows C_6H_5^+ + H_2 \qquad k = 6.6 \text{ [Smyth, et al, 1982]} \qquad \text{(R9)}$$

$$C_3H_3^+ + C_4H_2 \rightleftarrows C_7H_5^+ \qquad k = 6.6 \text{ [Smyth, et al, 1982]} \qquad \text{(R10)}$$

Experimental investigations often demonstrated the occurrence of a specific reaction but did not give a measured reaction rate coefficient. In cases where both experimental and Langevin calculated rate coefficients are both available, they are in good agreement so when experimental data were unavailable, calculated rates were used with confidence. Prior to publication of the kinetic mechanism the literature will have to be surveyed again to make sure that the data are up to date. Fialkov [1997] has recently surveyed the subject of ions in flames and summarizes measurements of ionic reactions relevant to the subject.

IV. MASS SPECTROMETER SAMPLE CONE COMPLICATIONS

Stein [1983] suggested that mass spectrometrically identified flame ions may not be the ions in the flame but ions which have been formed by ion-molecule (specifically H atom addition reactions) reactions in the sampling cone, where the gases are cooled by expansion. Such a change in ion identity would not alter the original premise of ion growth through ion-molecule reactions, but would complicate the comparison of the model output with the experimental mass spectral data. A new set of reactions and ions would have to be added to the mechanism in order to relate the observed ions to the parent ions present in the flame. Many of the observed ions are more stable at high temperatures than the parent ion. Thus, e.g., the observed $C_{14}H_{11}^+$ ion might be the result from a shift in the equilibrium with the flame ion $C_{14}H_{10}^+$:

$$C_{14}H_{10}^+ + H \rightleftarrows C_{14}H_{11}^+ \qquad \text{(R11)}.$$
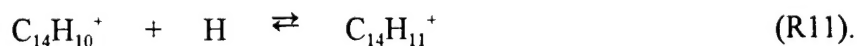
When it was first proposed that flame ions might change their identity through rapid ion-molecule reactions in the sampling cone, this possibility was examined in terms of the rate of temperature drop during the expansion process inside the sampling cone using the current theoretical analysis of such process, and it was concluded that the rates of hydrogen atom addition reactions were small, although not necessarily negligible. Because of the complications involved in relating the observed ions to the ions that actually existed in the flame, modeling was continued comparing the results with only experimentally observed ions. Later, based on our experience of the model giving good agreement

with experiment when the temperature in the model was reduced below experimental values, we examined possible aerodynamic cooling effects of the sampling cone on the incoming sampled gas stream upstream of the nozzle, as opposed to the earlier considerations of cooling in the expansion section downstream of the nozzle throat.

This treatment assumes a boundary layer at the prober cone entrance through which energy is transferred from the approaching gas stream to the probe cone, thus cooling the sampled gas. Choked flow is also assumed in the cone entrance to calculate the rate of gas flow through the sampling cone. Sampling is not isokinetic, so that a region in front of the nozzle, in which the flow is accelerated and the gas temperature is reduced, is affected by the probe. This distance, for the specific nozzles and operating conditions of interest, extends between 0.05 and 1.0 mm upstream of the entrance orifice. This distance corresponds to a time of between 2 and 4 X 10^{-5} s and a temperature drop from flame temperature, 2,000 K, to the sample cone temperature of about 1200K.

For fast ion-molecule reactions, this rapid change in temperature is still slow enough for the reactions to proceed to the extent that the sampled ions can differ from the ions in the flame. When the boundary layer effect was incorporated in the model, several types of phenomena were predicted in the boundary layer, governed largely by the thermochemistry of the reactions. The equilibrium $C_3H_3^+ \rightleftharpoons H_3C_3^+$ (linear to cyclic) is shifted far to the right, Fig. 2. The linear isomer is considered more reactive. Some ions react to produce completely different ions, e.g. $C_{12}H_8^+ + H\cdot \rightleftharpoons C_{12}H_9^+$ which, at decreasing temperature is driven to the right despite a reduction in entropy. In other cases the ion concentration may increase or decrease in the sampling region, e.g. $C_{21}H_{11}^+$ and $C_{19}H_{11}^+$. Cooling of the sampled gas provides an explanation as to why, in previous calculations, the temperature profile had to be artificially lowered to force agreement between experiment and model. This picture of such a dramatic sampling cone boundary layer effect on the observed ions would certainly change the description of the flame chemistry in the present high temperature acetylene / oxygen flame. Further work is required to more accurately define the effect.

V.   COMPUTER MODEL

The Sandia flame code was modified for this program by Prof. Fokion N. Egolfopoulos (USC) to accommodate ions. After using the program for several years, some problems were recognized, and some desirable additions were identified and the code modified accordingly. The means of treating ion and electron diffusion via ambipolar diffusion was improved but there remain some questions about the accuracy of the way ion, electron diffusion is treated. Recent additions to the code include: accounting for negative ion formation by electron attachment and removal of negative ions by recombination with positive ions. In addition, as pointed out in Section III, the chemical mechanism now starts with the chemiionization reaction rather than starting with two ions input in the form of concentration profiles.

Two new techniques were thus used to obtain a more reliable calculation using the ionic mechanism to account for the observed appearance of large concentrations of ions in fuel rich hydrocarbon flames. These two techniques were: (1) correction of the mass spectrometer

measurements for sampling probe interference, and (2) including chemiionization by estimating the profiles of two species, CH* and O atoms, for which experimental data in the system of interest are unavailable.

VI.   COMPARISON OF MODEL WITH EXPERIMENT

The results of a calculation incorporating chemiionization and nozzle cooling are presented in Fig. 3 in which maximum experimental and calculated ion concentrations are compared. The maximum CH* (electronically excited CH) concentration assumed for this calculation was 1.0×10^{-6} mol fraction and assumed to occur at 8.5 mm above the burner, the full width at one percent of the maximum was 2.5 mm.. The ion $C_4H_5^+$, which always calculates higher by more than two orders of magnitude, was not included in Fig. 3. It is not clear why this large discrepancy is also observed for $C_4H_5^+$. The agreement, without $C_4H_5^+$, is excellent and far more impressive than that obtained by neutral species modeling, e.g. Frenklach and Warnatz [1987].

VII.   WHY A SHARP THRESHOLD FOR SOOT FORMATION?

Since the soot threshold is a very well defined property of any hydrocarbon oxygen (air) mixture, it is expected that at soot threshold those reactants responsible for soot formation, e.g. PCAH, would show a dramatic change in concentration. In a review of the literature it was demonstrated that the only flame characteristics that correlate with the soot threshold are ion concentration and, more dramatically, the ion identities. After presentation of this topic at the 1995 AFOSR meeting and at the Eastern States Meeting [Calcote and Keil, 1995] someone in the audience quoted data which contradicted this observation. When the references were checked, one on OH concentrations [Inbody, 1992] and the other on PCAH concentrations [Bittner, J. D, 1981], the references respectively indicated that there is no change in concentration of OH or PCAH at soot threshold.

There are two questions: are the changes in ion concentration a cause or an effect of soot formation? and, why does the ion concentration and composition of the ions change so dramatically? These questions are being considered. Because ionic growth reactions are inversely proportional to temperature due to thermochemistry (see section VIII), the possibility that temperature is involved has been considered The adiabatic flame temperature, and experimental flame temperatures, to the extent available, both decrease smoothly with increasing fuel to oxidizer ratio, C/O, through soot threshold. The standard acetylene / oxygen flame is different, both temperatures show a small drop at soot threshold. A major complication has to be recognized: the standard flame on which most studies have been made is an acetylene / oxygen flame where soot first appears at C / O =1.0. This is where it is expected to appear on stoichiometric / thermochemical grounds [Calcote and Keil, 1995]. In fact, in this flame the measured soot concentration is actually less than predicted by thermochemical equilibrium. Not only does the adiabatic flame temperature remain essentially constant with C / O for the acetylene flame, but the measured temperature does also, both showing only a small drop at soot threshold!

It has been argued by a number of people [Delfau et al, 1979, Haynes and Wagner, 1981, Haynes, 1991] that the increase in ion concentration at soot threshold is due to the formation of ions from soot particles. Based on the data, this assumption is logical, especially when one has a predilection for a free radical mechanism. This assumption, however, is difficult to defend [Calcote et al, 1988] because of the thermochemical barrier to the proposed process:

$$S^+ + M = S + M^+ \qquad \qquad \text{(R12)}$$

where S^+ and S are a charged and uncharged soot particle, and M and M^+ are a neutral and a charged molecular species. The ionization potential for soot particles is size dependent, between 4.6 eV for bulk carbon and 5.4 eV for 2 nm particles [Calcote, 1981]. Ionization potentials for large molecules to small molecules, like acetylene range from about 6.5 to 11 eV [Lias et al]. Thus, at the extremes, reaction 5 is endogenic by 1.1 to 6.4 eV (106 to 618 kJ/mol). The low extreme (1.1 eV) involves small particles with large ionization energies, which will be little ionized, and large neutral species, for which the concentrations are small. There is thus no driving force to produce ions from charged soot particles. This scenario has also been rejected by Gerhardt and Homann [1990] as unrealistic because of energetic considerations.

The scenario that PCAH anions form at soot threshold removing electrons and thus reducing the rate of cation decay was also examined in this program. Cation - anion recombination is about 100 times slower than cation - electron recombination. The slower removal of cations in cation - anion recombination could increase the cation concentration. It was found that the concentrations of both large PCAH and electrons are too small to account for the number of anions that would be required to account for the increase in soot concentration. By analogy, the possibility was also considered that electron attachment to soot particles might affect the cation composition by substituting cation - negatively charged particle recombination for cation - electron recombination. This rate would be even slower than that for cation - anion recombination It turned out that thermal ionization of soot particles was more important in determining the charge on soot particles than electron attachment.

The cause of a sharp soot threshold is still not identified. This remains a major challenge for the soot community.

VIII.   ENERGY TRANSFER RATES IN ION- MOLECULE REACTIONS

In considering possible explanations of why reducing flame temperature in the model from the measured value, 2000 K, to 1700 K gave closer agreement with experiment, the possible effects of energy transfer on ion-molecule reaction rates were considered. The question was: how fast does a flame ion, produced with excess energy in an exergonic (negative Gibbs energy) ion-molecule reaction, lose its energy to the bath gas, (i.e. equilibrate its internal temperature with the flame gases) compared with the rate at which the product ion reacts in another ion-molecule reaction?

The rate at which a large molecule, e.g. azulene, transfers excess vibrational energy to a variety of bath gases has been extensively studied [see e.g. Clarke et al, 1992, Shi and Baker, 1988,

and Hipple et al, 1985] so these results can be used to estimate the rate at which large ions lose energy to the flame bath gas. The objective of this exercise is to determine whether or not this phenomena requires attention in considering a sequence of exergonic ion-molecule reactions such as occur in fuel rich flames.

It is appropriate to apply thermochemical analysis to a kinetics problem involving ion-molecule reactions because ion-molecule reactions occur at every collision, as verified by the observation that at low temperatures (there are no data at high temperatures) Langevin rates agree with experimental rates. Exergonic ion-molecule reactions generally do not have an activation energy, but the net forward reaction rate is determined by the difference in the forward reaction rate and the reverse reaction rate, consistent with the theory of microscopic reversibility. Meot-Ner (1991) discusses in great detail the relevance of thermochemistry to ion-molecule rates for reactions. His arguments on proton transfer ion-molecule reactions should apply in general to ion-molecule reactions especially to those in which Langevin rates have been confirmed experimentally. Meot-Ner defined a reaction efficiency, r, as the ratio of the measured reaction coefficient, k_f, to the collision rate coefficient, k_c. The reverse reaction coefficient, k_r, is reduced by the thermochemical factor, thus:

$$k_r = k_{cr} \exp (-\Delta_r G / RT) \tag{4}$$

where k_{cr} = the collision rate for the reverse reaction.

The Gibbs energy acts as an activation energy when it is positive. Thus when $\Delta_r G$ is positive, excess vibrational energy will reduce the effective activation energy. Meot-Ner demonstrated that for reactions, when there is no energy barrier, i.e. no activation energy other than that due to thermochemistry, the sum of the forward and reverse reaction efficiencies (r_f and r_r, respectively) is approximately equal to one :
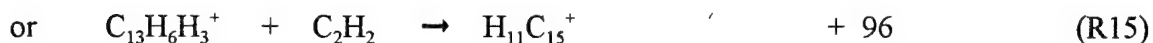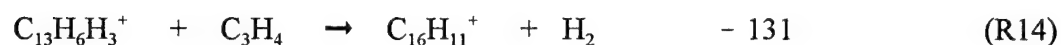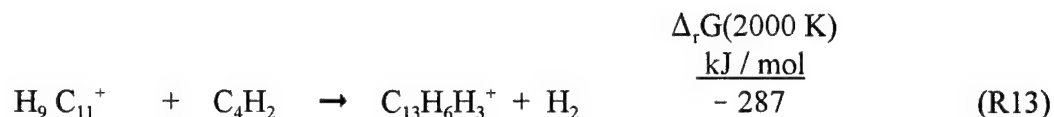
$$r_f + r_r \approx 1 \tag{5}$$

The two processes: (1) energy transfer from vibrationally excited ions to the bath gas, and (2) ion-molecule reactions were compared through their relaxation times. The relaxation time for vibrational energy exchange with the bath gas is:

$$\tau_e = 1 / k_e N \tag{6}$$

where k_e is the rate coefficient to remove an average quantum of vibrational energy, $<E>$, and N is the concentration of the bath gas constituents removing energy. The term $<E>$ has been measured by Hippler et al (1985) and Shi et al (1988) for vibrationally excited azulene in many gases, including CO and H_2. CO and H_2 values of $<E>$ for azulene excited with 200 kJ / mol energy were weighted by their mol fraction in the standard C_2H_2 / O_2 flame to give $<E> \approx 1.7 \pm 0.16$ kJ / mol. This value has been demonstrated to scale linearly with excitation energy. [Shi et al, 1988].

To make this discussion more relevant to the specific interests of this program, three typical reactions[1] from the proposed mechanism are considered.

$$\Delta_r G(2000\ K)$$
$$kJ\,/\,mol$$

$$H_9\,C_{11}^{+} \quad + \quad C_4H_2 \quad \longrightarrow \quad C_{13}H_6H_3^{+} + H_2 \qquad\qquad -287 \qquad\qquad (R13)$$

$$C_{13}H_6H_3^{+} \quad + \quad C_3H_4 \quad \longrightarrow \quad C_{16}H_{11}^{+} \quad + \quad H_2 \qquad\qquad -131 \qquad\qquad (R14)$$

or $\quad C_{13}H_6H_3^{+} \quad + \quad C_2H_2 \quad \longrightarrow \quad H_{11}C_{15}^{+} \qquad\qquad\qquad +96 \qquad\qquad (R15)$

The energy from the forward reaction R13 will reside in both the products $C_{13}H_6H_3^{+}$ and H_2. The fraction of the 287 kJ / mol Gibbs energy released in the product hydrogen will be small and will rapidly dissipate to the bath gas. The question is what are the relative rates for dissipation of the excess energy in $C_{13}H_6H_3^{+}$ to the bath gas and the subsequent reactions R14 and R15.

The number of collisions, X, required to transfer all of the energy to the bath gas is simply the excess energy to be transferred, divided by the energy transferred per collision. Thus for reaction R13 at 2000 K, assuming all of the energy is deposited in the $C_{13}H_6H_3^{+}$; $X \approx 287\,/\,1.7 \approx 169$ collisions. The characteristic collision time for the number of excited species collisions with the flame gases in which energy can be transferred is assumed to be the same as in Equation 6:

$$\tau_c^{*} = 1\,/\,k_c^{*}N \tag{7}$$

where k_c^{*} is the rate coefficient for the excited ion colliding with a bath gas at concentration N. For k_c^{*} the average of rate coefficients for measured ion-molecule reactions R5 to R10 was used, i.e. $8 \times 10^{14}\ cm^3\ mol^{-1}\ s^{-1}$ ($1.3 \times 10^{-9}\ cm^3\ molecule^{-1}\ s^{-1}$), and N is the total concentration of molecules, $9.7 \times 10^{16}\ cm^{-1}$. For the present low pressure flame, $\tau_c^{*} = 7.9 \times 10^{-9}$ s, yielding a total energy transfer time, τ_E :

$$\tau_E = X\,\tau_c^{*} = 1.3 \times 10^{-6}\ s \tag{8}$$

This time is compared with a characteristic time for a typical ion-molecule reaction:

$$\tau_c = 1\,/\,k_f\,N_r = 9.6 \times 10^{-8}\ s \tag{9}$$

where: N_r is the sum of the major reactants, C_2H_2 and C_4H_2, concentrations, i.e 8×10^{15} molecules cm^{-1}, and k_f is assigned the same value as k_c^{*}..

This rather crude calculation indicates that the time for reaction is less than the time to equilibrate with the bath gas, by a factor greater than 10, so that excess vibrational Gibbs energy will accumulate in the growing ions. This situation is not expected to be as important in neutral reactions

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[1] The order of C and H indicate a specific isomer.

because the energies involved are less and the reaction rates are less. Thus for R13 the energy in $C_{13}H_6H_3^+$ can increase the reverse reaction rate, and thus decrease the net forward rate of R13. It cannot increase the forward rate of R14, which is already sufficiently exergonic to occur on every collision. The excess exergonicity of R13 could, however, increase the forward rate of R15 by reducing the ergonic barrier of R15. Reaction R15 is an example of a typical reaction that would go forward at lower temperatures, but because of entropy effects this condensation reaction's forward driving force is reduced as the temperature is increased; e.g. $\Delta_r G = -96$ and $+0.2$ kJ / mol at 300 and 1500 K, respectively.

Clearly, excess energy cannot build up indefinitely in a series of reactions. While some of it will be dissipated to the bath gas, at some point the excess energy will cause the growing cation to dissociate, e.g.:

$$C_{16}H_{11}^+ \rightarrow C_{12}H_9^+ + C_4H_2 \tag{R16}$$

The above energy accumulation phenomena could have a critical effect on those reactions which have negative Gibbs energy at lower temperatures and positive Gibbs energy at higher temperatures due to sensitivity to the entropy factor. Reaction R15 is a typical example of such a reaction. The accumulation of energy could also open up other reaction channels for reactions having energy barriers. The inclusion of energy accumulation in the computer model could greatly alter the calculated temperature effect which has caused so much trouble in this program.

Even recognizing the many approximations made in this analysis, it should be clear that energy accumulation in a series of ion-molecule reactions may have a significant effect on the ion growth chemistry in the sooting flame modeled here. A more detailed analysis is warranted but it is clearly complicated and beyond the scope of this study.

IX. THE RELATIVE IMPORTANCE OF AN IONIC OR NEUTRAL REACTION MECHANISM IN TURBULENCE MODELS OF SOOT FORMATION

The two most poorly understood processes in combustion science are turbulent combustion and soot formation. Most practical combustion systems involve turbulent flames. To understand and predict soot formation in practical combustion systems, it is important to understand how combustion and turbulence interact. It would also be important to know, in modeling soot formation in a turbulent flame, whether choosing a neutral (free radical) or ionic mechanism of soot formation would make any significant difference in the final result of the model study. Two possible reasons why the choice might be important are identified and discussed here. The first relates to the electrical nature of the system when the ionic mechanism is used, and the second relates to a difference in the chemical reaction rates for a free radical or an ionic mechanism.

Physically, it is easy to see some unique phenomena associated with an ionic mechanism of soot formation in a turbulent flame. Free electrons are produced in the initial chemiion step, and these remove cations by direct recombination with them, or through attachment to neutral species to produce anions which remove cations by recombination with them. Distortion of the flame sheet or

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flamelet surface can enhance electron diffusion away from the environment in which the electrons were produced. This would increase the local cation concentration and thus enhance the soot formation process. The significance of this has yet to be quantified. Increased cation concentration should also cause the flame sheet or flamelet to take on a positive charge. Whether this charge will be sufficient in affecting the interaction between flame sheets or flamelets has yet to be determined.

Turbulent flow and combustion chemistry are each characterized by a broad spectrum of length and time scales (they are related through a velocity), and the ratio of either of these scales for the turbulence and chemistry indicate the effect of turbulence on the chemistry and visa versa. There is some preliminary evidence that the chemical characteristic time scales for the free radical and ionic mechanism are different [Calcote and Gill, 1994], Table 1. The standard means of determining the relative importance of fluid flow and chemistry is through a Damkohler number, D = fluid flow characteristic time / chemistry characteristic time. When $D \gg 1$, chemistry is unimportant, and when $D \ll 1$ or about 1, chemistry must be considered. To determine whether the choice of a free radical or ionic mechanism is important, it is necessary to determine whether D is significantly different for the two mechanisms and, at the same time, is not $\gg 1$.

Soot formation is a complex process that occurs in laminar flames after the maximum temperature is reached. A series of steps are involved in a sooting flame: (1) the unburned gas is preheated; (2) heat releasing chemistry occurs; (3) soot precursors (free radicals or the chemiion $HCO^+)$ necessary for initiating the nucleation process are formed; (4) soot nucleation occurs by the growth of the precursors to large polycyclic aromatic hydrocarbons (neutral or ionic); (5) coagulation to even larger PAHs occurs; (6) soot forms; and (7) soot grows by addition of smaller species, by coagulation and by agglomeration. The premise of the discussion below is that after the coupled steps, (1) and (2), the subsequent steps are independent of each other, except that (3) must follow (2), (4) must follow (3), etc. Except for steps (1) and (2) the steps do not need to be contiguous in time or space. Step (3) will most likely overlap step (2) because the fast chemistry occurring in this step produces the supra-equilibrium species (e.g. hydrogen atoms and HCO^+) that are necessary for soot formation, depending upon a whether a neutral or ionic mechanism is assumed. The combined steps (1) and (2) or the zone in which these steps occur, will be referred to as the "classical flame" To determine whether the chemistry associated with any one of the individual steps will be influenced by the turbulent structure or visa versa, the characteristic time or distance associated with the chemistry involved in that individual step must be compared with the characteristic time or distance in the relevant elements of the turbulent field.

Numerous theoretical approaches to understanding the interrelationships between chemistry and turbulence have been proposed [see e.g. Williams, 1985, Bradley, 1992, Bray, 1996, Poinsot, 1996]. The problem becomes especially complicated when soot is present [Kent and Honnery, 1987, Magnussen, 1974]. A physical picture of how chemistry and turbulence interact was described by Howe and Shipman [1965]. In their picture, the burning zones of a turbulent flame consists of parcels (eddies) of unburned gas that are dispersed throughout a burned gas, or the reverse, with burning at the periphery of the parcels by a reaction zone or flame similar to a laminar combustion wave. The size distribution of the parcels is governed by splitting of the parcels by shear flow and by combustion so that the reacting parcels become smaller and smaller with time. As the eddies eventually become too small to distinguish from diffusive mixing, the combustion process is described as a stirred reactor. More recent descriptions are similar to this, but involve wrinkled flame fronts [Williams, F.

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A., 1985]. The real challenge has been to incorporate the physical concepts of gas parcels, eddies and wrinkled flame fronts into a mathematical model which can also handle complicating phenomena such as flame stretch [Magnussen and Hjertager, 1976, Williams, F. A., 1985, Bradley, 1992, Poinsott, 1996 and Bray, 1996].

Williams [1985] and others [e.g. Bray, 1986] discuss turbulent combustion in terms of non-dimensional numbers. These are defined intuitively and are mostly theoretical constructs. There are essentially only four fundamental quantities: (1) the intensity of turbulence, (2) the scale of turbulence, (3) the laminar burning velocity, and (4) the flame thickness. These can be used to obtain characteristic times and lengths and to define a large number of non-dimensional numbers. The chemical characteristic time, τ_c, is defined as δ / S_u, where δ is the flame thickness and S_u is the laminar burning velocity. The flame thickness includes a preheat zone and a chemical reaction zone (steps 1 and 2). The chemical reaction zone which occurs near the peak flame temperature is much smaller than the preheat zone. Thus, the calculation of chemical time, τ_c, is essentially a calculation of the time associated with the preheat zone. Thus, e.g. Poinsot et al [1996] define the flame thickness, δ, as $(T_b - T_u) / (dT/dx)_{max}$, where T_b and T_u are the burned gas and unburned gas temperatures. τ_c is still defined as δ / S_u. Inherent in the concept of flame sheets and flamelets is the assumption that τ_c is less than some characteristic turbulence time scale. The implication is that chemistry is unimportant. Identification of τ_c as δ / S_u is meaningful because the two zones are coupled.

Intuitively, chemistry must be more important in a turbulent flame than implied above. A turbulent flame is very different from a laminar flame. A laminar flame is defined as a plane combustion wave propagating into an unburned gas with a velocity, S_u, orthogonal to the combustion wave and relative to the unburned gas. In a turbulent field the flame sheet is strongly affected by: non-unity Lewis numbers; non-constant viscosity and heat losses; flame stretch; and flame curvature. In direct numerical simulation, DNS, an attempt is made to account for these effects [e.g. Poinsot et al, 1991, Poinsot et al, 1996 and Veynante et al, 1997]. The assumptions and conclusions in DNS studies [e.g. Poinsot et al, 1991, Poinsot et al, 1996 and Veynante et al, 1997] seem intuitively reasonable and appear to be consistent with experiment. The flame sheet is distorted by eddy action which may produce convex or concave surfaces. Because of resulting gradients in Lewis number and viscosity through the flame, the flame must now be treated as an onion in which each layer must be treated differently. Subsequently, the flame sheet is stretched to the quenching point and flamelets are generated. In a highly distorted flame the laminar burning velocity must have very little meaning and the chemistry should become more important.

The descriptions of what happens when turbulent eddies interact with a flame are instructive but further study is required to answer the basic question: would there be a significant effect on the predicted quantity of soot formed depending upon whether a neutral or ionic mechanism were used? The interaction of soot formation chemistry with turbulence can differ greatly from the situation when the chemistry serves only as a heat source to propagate the flame. In the classical flame, the chemistry and preheat zones cannot be separated, they are coupled. In contrast, soot formation processes may not need to be coupled. Thus, if a burning eddy were quenched prior to completion of the soot forming process, and subsequently mixed with gas containing appropriate reactants or conditions (e.g. temperature) required for soot growth, the growth process may pick up where it left off. Even if the life of an eddy or flamelet, where the soot process was first initiated, were long

compared to the soot forming time scales, strongly curved surfaces, stretch, and varying Lewis numbers from the unburned side to the burned side of the reaction zone requires that each layer of the reaction zone be treated separately. In this case the individual soot forming steps may still be important and the quantity of soot produced could depend on whether an ionic or free radical mechanism is used. An appropriate Damkohler number may still be relevant for the above situations.

To help answer the question, "does it make a difference whether a neutral or ionic mechanism is used to model soot formation in a turbulent flame?", numbers, which can be used to define an appropriate Damkohler, or other appropriate number, are required. The specific numbers required relating to a realistic turbulent environment are: flow time through a flame front, a characteristic time for the flamelets (e. g. life time), and rates of changing curvature and stretch. The specific numbers required for the chemistry are the characteristic times for the various steps in the soot formation process for both the free radical and for the ionic mechanism. The fluid dynamic numbers are being pursued by evaluation of both experimental data and published theoretical analysis, especially DNS. For the steps in the soot formation process the sources of information are the computer models of soot formation and experimental profiles of temperature, and species (neutral, free radical and ion) concentrations in flames.

The basic question of whether the time scales related to soot formation by either the free radical or ionic mechanism can be slow compared to practical turbulent time scales is still unanswered. We are pursuing a quantitative answer.

X.   PUBLICATIONS AND PRESENTATIONS

1   "Comparison of the Ionic Mechanism of Soot Formation with the Free Radical Mechanism" Calcote, H. F. and Gill, R. J. in Soot Formation in Combustion, H. Bockhorn, ed., Springer-Verlag 1994, pg. 471 - 484

2.   "Why a Sharp Soot Threshold?", Calcote, H. F. and Keil D. G., Presented at The Eastern States Section Meeting of the Combustion Institute, Worcester Polytechnic Institute, Worcester, MA, October 16-18, 1995.

3.   "Thermochemistry of Cations", Calcote, H. F. and Gill, R. J. in preparation for J. Phys. Chem.

4.   "An Ionic Mechanism for Cation Growth in Fuel Rich Flame", Calcote, H. F. and Keil, D. G. in preparation for Comb and Flame

5.   "Fluid Mechanical Effects on Mass Spectrometer Sampling of Flame Plasma", Berman, C. H., Keil, D. G, and Calcote, H. F. in preparation for Comb and Flame

6.   "The Growth of Cations and Soot Formation in Acetylene / Oxygen Flames", Calcote, H. F., Keil, D. G. and Egolfopoulos, E., in preparation for Comb and Flame

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7. "In Defense of The Ionic Mechanism of Soot Formation" Calcote, H. F. and Keil D. G., Presented at The Eastern States Section Meeting of the Combustion Institute Hilton Head, SC, Dec.9 - 11, 1996, in preparation for submission to Comb and Flame

8. "The Relative Importance of An Ionic or Neutral Mechanism on Turbulence Models of Soot Formation", Calcote, H. F. in preparation for submission to Comb and Flame Brief Communications

9. "Dusty Combustion Flame Plasma", Calcote, H. F. Invited Presentation at Workshop on "Dusty Plasmas" held at The Harvard-Smithsonian Center for Astrophysics, May 15 to 17, 1997

10. "Ions in Flames - Sources, Reactions and Sinks", Calcote, H. F. Invited Presentation at JANAF Combustion Subcommittee Workshop on "Diagnostics of Plasmas and Their Effects on the Chemistry of Solid Gun Propellants" ARL, Aberdeen MD 6 to 7 May 1998

11. "Problems in Modeling High Temperature Ion Growth", Keil, D. G., Berman C. H., and Calcote, H. F., Poster, Work in Progress, Twenty Seventh Symposium on Combustion., Boulder CO, August 1998

XI. HONORS / AWARDS

Dr. Calcote was awarded the Sir Alfred Egerton Gold Metal by the Combustion Institute for "distinguished, continuous and encouraging contributions to the field of combustion". Especially highlighted in the presentation was his work on ions in flames, identifying the mechanism of chemiionization, and his studies of the growth of ions in fuel rich flames and their influence on soot formation, the subject of this AFOSR program..

XII. INVENTIONS

None.

XIII. TECHNOLOGY TRANSITIONS

H. F. Calcote, ChemIon, Inc., 609 716-1201 x 42: transfer of flame ion science by designing and performing an experiment to demonstrate the possible use of dc and ac electric fields to stabilize and enhance mixing in a large combustor, for Stan Sattinger, Westinghouse Electric Corporation, Science and Technology Center, Pittsburgh, PA, phone 412 256-2637.

XIV.   ACKNOWLEDGMENTS

XV.   REFERENCES

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Table 1, Comparison Of Characteristic Times for Neutral and Ionic Mechanisms For Soot Formation

Data from models (Calcote and Gill, 1994)

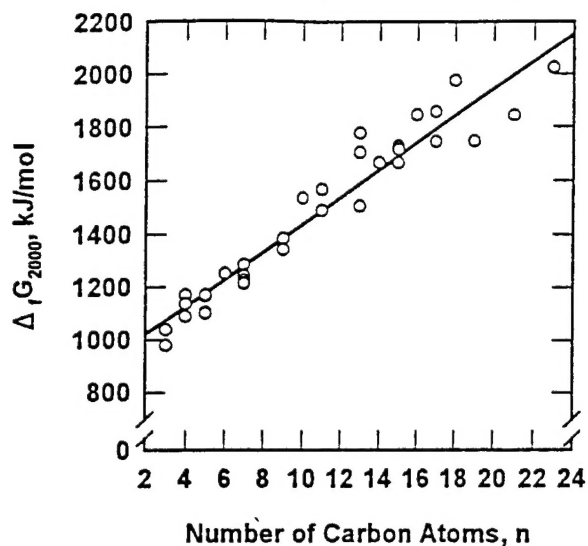|	Neutral	Ion	Neut /Ion
To add one carbon atom, μs	0.82	0.65	1.25
Number reactions to add 10 Carbon Atoms	10	5	2.0
Average time / step, μs	0.82	1.3	0.63
Time per step, Min. to Max. μs	0.01 - 3.2	0.50 - 3.6	0.02 - 0.89
Initial Step, μs			
$C_3H_3 + C_3H_3 \Rightarrow C_6H_6$	7		
$CH^* + O \Rightarrow HCO^+$		600	0.012
Growth to Coronene, 300 u	250	200	1.25
Growth to mass 500 u	410	325	1.25

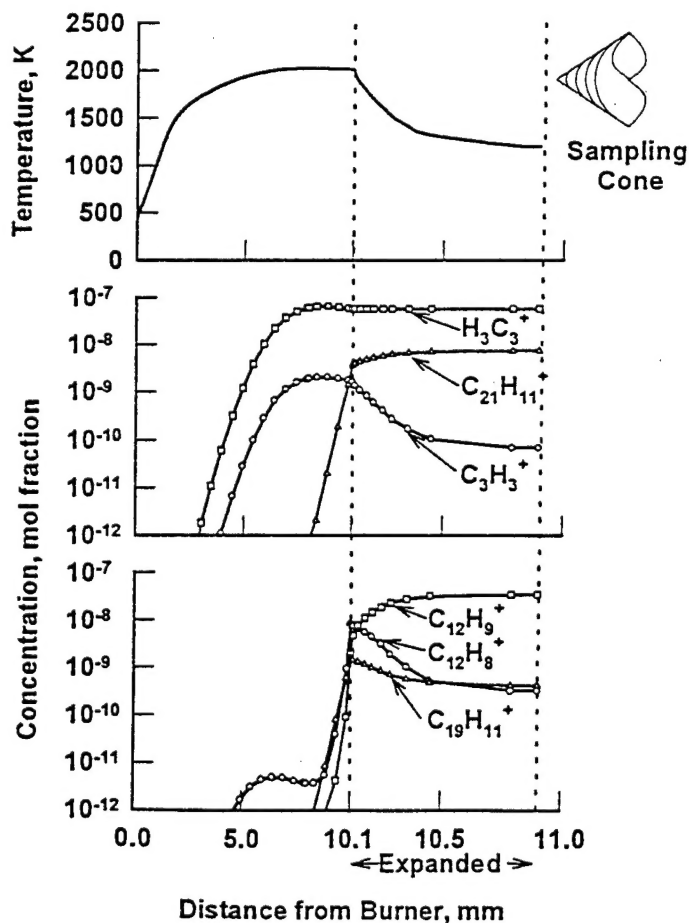Figure 1 Correlation of Gibbs Energy of Formation with Carbon Number for Cations at 2000K

Figure 2 Typical Calculated Profiles Showing Effect of Sampling Cone Acetylene - Oxygen Flame at $\Phi = 3.0$ $P = 2.67$ kPa and $u = 50$ cm/s
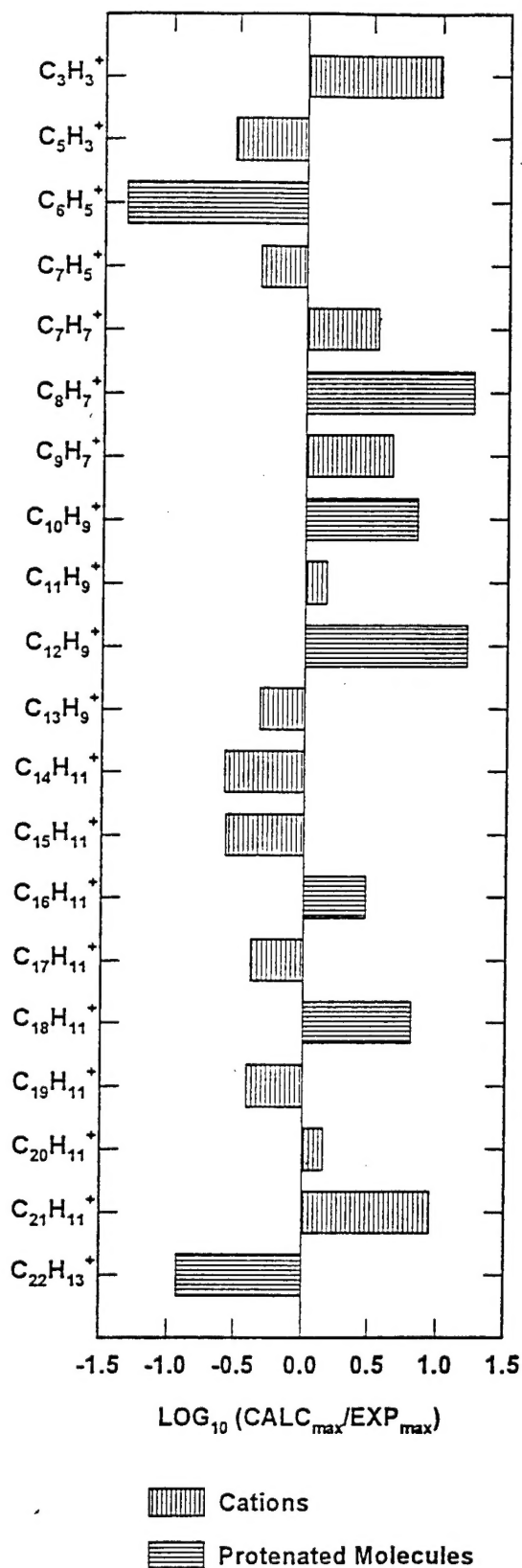

LOG$_{10}$ (CALC$_{max}$/EXP$_{max}$)

Cations

Protenated Molecules

Figure 3 Comparison of Calculated (CALC)$_{maximum}$ and Experimental (EXP)$_{maximum}$ Cation Concentrations

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